Solvent Extraction of Tar Acids From Various Sources

D. C. Jones and M. B. Neuworth

Consolidation Coal Company
Research and Development Division
Library, Pennsylvania

Solvent extraction of tar acids from tar acid containing oils is of interest because of the potential savings in investment and operating costs over the conventional batch caustic extraction process. A relatively large number of solvents have been evaluated for this purpose. For the most part, preferred solvents contain a polar oxygen group[1] and include water, methanol, ethanol, formic acid, acetic acid, glycerine, triethylene glycol, and diethanolamine[11]. Most of the previous studies involved countercurrent extraction with a single solvent. At high tar acid recovery levels, there is a significant carryover of neutral oil, requiring secondary purification of the polar solvent extract. Fractional extraction with two solvents provides a technique for the recovery of one component of a mixture both in high yield and in high purity.

Aqueous methanol-hexane were investigated in our laboratory[6] as a solvent pair, based on their high selectivity for tar acids, low cost, ease of recovery, and stability. The yield and quality of tar acids produced by solvent extraction of the three most important commercial sources, coke oven tar, petroleum derived cresylic acids, and low temperature tar will be discussed. In addition, separation of tar acid isomers and homologues by solvent extraction will be described.

Experimental

Extraction studies were carried out in a 1" x 8' extraction column of the Scheibel type. A schematic diagram of apparatus is shown in Figure 1. The solvents, aqueous methanol and hexane were stored in 5-gallon borosilicate bottles. Gravity feed was used, flow rates being measured with rotameters. The temperature of the solvents was maintained by passage through coils heated or cooled in a water bath. Tar acid oil was pumped into the extraction column by means of a precision motor driven syringe. The tar acid oil feed point was the sixth stage of the twenty-eight stage extraction column. The methanol extract was freed of solvent by distillation on a 1" x 4' Vigreaux column. The residue consisted of a mixture of water and refined tar acids. The water was separated by decantation and analyzed for dissolved tar acids by butyl acetate extraction. The wet tar acids were analyzed for water, neutral oil, and pyridine bases by standard methods. In the case of the tar acids derived from petroleum, aromatic thiols and disulfides were determined[5]. The hexane raffinate was similarly distilled. The solvent free residue was analyzed for tar acids by a modified caustic contraction method.

The detailed procedure for laboratory scale refining of a methanol extract with anion and cation exchange resins has been described[6].

Discussion

Low Temperature Tar Acids

A tar acid oil (b.p. 160-230) derived from fluidized low temperature carbonization of a Pittsburgh Seam coal was refined with aqueous methanol-hexane. Previous studies[8] narrowed the optimum concentration of methanol to 60 to 70%, using feed:methanol:hexane ratios of 1/1.5/3.0. The extraction conditions and results are shown in Table 1. The observed recovery of tar acids in the methanol extract was 92%. Neutral oil contamination was 0.08%, well below the acceptable level for commercial tar acids.

Tar base content was determined as 0.6%, which is 3 to 6 times higher than current specifications. This carryover of tar bases is a limitation of the solvent extraction approach to tar acid refining and is characteristic of all organic solvents considered to date. Removal of tar bases from tar acids by extraction with sulfuric acid or by distillation with sulfuric or phosphoric acids[1] has been proposed. An ion exchange technique, using a strong acid cation resin, for removal of tar bases from methanol extracts was developed in our laboratory and has already been described[2].

Low temperature tar acids produced by solvent extraction or caustic extraction are contaminated with small quantities of aliphatic acid, ranging from acetic through butyric acid. These aliphatic acids are concentrated in the phenol fraction and impart a foul odor. Purification of the methanol extract with an anion exchange resin and a cation exchange resin in series[2,7], results in the recovery of tar acids of satisfactory quality with respect to neutral oil, aliphatic acids, and pyridine bases.

A schematic flow diagram and the chemical reactions involved in this ion exchange purification are shown in Figure 2. The methanol extract is pumped over an anion exchange resin. The quaternary ammonium hydroxide groups combine with tar acids to form phenolate salts. The aliphatic acids by virtue of their higher acidity gradually displace the phenols until the resin is saturated with aliphatic acids. Breakthrough of aliphatic acids follows and regeneration is required. The methanol extract then contacts a cation resin where pyridine bases are removed as pyridinium sulfonates. The purified methanol extract is treated as before for the removal of methanol and water. The analysis of the fully refined tar acids is presented in Figure 2. The neutral oil and tar bases values of 0.08% and 0.05%, respectively, are well within commercial specifications. Aliphatic acids could not be detected by analysis or by odor.

Coke Oven Tar Acids

Solvent extraction of tar acids from coke oven tar presents a number of unique problems. A narrow boiling tar acid oil contains sufficient naphthalene to raise its freezing point well above ambient temperature, which necessitates diluting the tar acid oil with one of the solvents or extracting above ambient temperature. The concentration of tar acids is about 1/3 the concentration of the corresponding fraction from low temperature tar, and the ratio of tar bases is quite high, 0.11 as compared to 0.013 for low temperature tar acid oil. The low concentration of tar acids imposes an economic penalty, since throughputs and solvent ratios are proportional to the tar acid oil volume rather than absolute tar acid concentrations. The relatively high concentration of tar bases will result in a correspondingly large contamination of the recovered tar acids, since most

oxygenated solvents will extract pyridine bases. The detailed solvent extraction conditions and extraction results are shown in Table 2. A 90% recovery of tar acids was obtained. The neutral oil content of the recovered tar acids was well under 0.1%, which meets current specifications. The tar base contamination was 4.1% as compared to published specifications of 0.1 to 0.2%. Ion exchange purification would reduce the tar bases to an acceptable level. However, the costs for such a secondary purification would be quite high because the consumption of ion exchange regenerant is proportional to tar base concentration. The added refining costs might be justified if by-product credit could be taken for the tar bases, which can be recovered from the resin, free of tar acids and neutral oils.

Petroleum Cresylics

Crude tar acids produced by the caustic washing of gasoline have become an important source of refined cresylic acids in the U. S. Normally, these are available as caustic solutions containing 10 to 50% tar acids and from 1 to 20% aromatic mercaptans and disulfides. The conventional method of separating the sulfur compounds from tar acids is oxidation of the sulfur compounds to disulfides and separation of the caustic insoluble disulfides. While a significant purification can be effected, sufficient disulfides remain dissolved in the alkaline solution to be objectional, and there is a loss of tar acids during the oxidation step.

Fractional extraction of a feed of this type with aqueous methanol-hexane[8] under optimum conditions results in a recovery of 95% of the tar acids and simultaneous elimination of 99.5+% of the mercaptans and disulfides in the feed. The effectiveness of this separation is quite unexpected when one considers phenol and thiophenol as prototypes of the mixture. Although thiophenol is almost a thousand times stronger an acid than phenol, thiophenol is rejected by aqueous methanol, the more polar solvent. The distribution behavior of thiophenols can be explained as a result of their inability to hydrogen bond with oxygenated solvents.

The details of an actual laboratory extraction of a crude tar acid mixture from petroleum is shown in Table 3. Using a tar acid/60% methanol/hexane volume ratio of 1.0/2/4.5, the recovery of tar acids in the extract was 97% and the sulfur compound contamination was 0.012%. Neutral oil contamination is 0.05%. Tar acids derived from catalytic cracking of gas oils contain very low concentrations of pyridine bases because chemical combination of basic compounds with the acidic cracking catalyst occurs during cracking. Maximum pyridine contamination is about 0.05%, which is acceptable.

Pitt-Consol Chemical Company, a subsidiary of Consolidation Coal Company, has operated a commercial extraction unit for the refining of petroleum derived tar acids for 6 years. Composite crude tar acids from at least 35 petroleum refineries are being processed. The performance of the commercial extraction column duplicates our laboratory unit in terms of yield and purity of refined tar acids.

Miscellaneous Refining Applications

Separation of Monohydric - Dihydric Phenol Mixtures

Tar acids boiling above 230°C from low temperature tar contain dihydric phenols, which turn pink when alkaline solutions of the tar acids are oxidized.

This discoloration is objectionable when disinfectant applications are contemplated. Removal of the pinking components has been effected by air-blowing alkaline solutions or extraction with borax, requiring consumption of chemicals and loss of some tar acids due to oxidation.

Fractional solvent extraction of the high boiling tar acids (230-350°C) produced from low temperature tar with more dilute methanol-hexane[10], will separate the dihydric phenols. The results are summarized in Table 4. Using 30% methanol, 11% of the feed is recovered as a methanol extract, the raffinate boiling up to 260°C containing no dihydrics. An increase in the methanol concentration to 35% removed more of the dihydrics, the tar acids boiling up to 280° being free of pinking. When the methanol concentration was increased to 40%, a hexane raffinate of 79% was obtained, which showed no dihydrics in the tar acids boiling up to 300°C. Extraction of a synthetic mixture containing 50% catechol with 35% aqueous methanol-hexane produced a hexane raffinate, containing 76% of the monohydric phenols completely free of catechol. This method has the advantage of complete recovery of tar acids in two fractions, one of which contains no dihydric phenols.

Separation of 2,6-Xylenol From Mixed Cresols

An interesting application of aqueous methanol-hexane extraction is the separation of 2,6-xylenol from mixed cresols. 2,6-Xylenol occurs in low concentrations in the cresol fraction and is very difficult to recover in high purity because it boils quite closely to both o-cresol and m,p-cresol.

Fractional extraction of a mixture corresponding in composition to a fraction boiling between o-cresol and m,p-cresol was tried, using dilute methanol-hexane[9]. The results are presented in Table 5. When 45% methanol was tried, 2,6-xylenol was recovered in 63% yield and 67% purity. Dilution of the methanol to 35% resulted in increased selectivity, and 2,6-xylenol was recovered in 91% purity and 54% yield. It would require several precision distillations to accomplish the same result. Apparently, aqueous methanol, when sufficiently diluted, can separate tar acids on the basis of both acidity and molecular weight.

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Table 1

Solvent Extraction of Low Temperature Tar Acid Oil

Feed Composition (B.P. 160-230°C)

	Wt.%
Tar Acids	44.5
Neutral Oil	54.8
Tar Bases	0.6
Aliphatic Acids	0.2

Extraction Conditions

	Vol. Ratio
Tar Acid Oil	1.0
60% Methanol	1.5
Hexane	3.0

Composition and Yield of Methanol Extract

Yield of Tar Acids 92 Wt.%

	Purity (Wt.%)
Neutral Oil	0.08
Tar Bases (Pyridine)	0.58
Aliphatic Acids (Butyric Acid)	0.36

Table 2

Solvent Extraction of Coke Oven Tar Acid Oil

Feed Composition (170-230°C)

	Wt.%
Tar Acids	14.3
Naphthalene	60.1
Neutral Oil	24.0
Tar Bases	1.6

Extraction Conditions

	Vol. Ratio
Tar Acid Oil	1.0*
70% Methanol	1.0
Heptane	3.0**

Purity of Tar Acids

	Wt.%
Neutral Oils	< 0.1
Tar Bases	4.1

*Fed as a 1:1 solution in heptane.
**Includes heptane used to dilute tar acid oil.

Table 3

Solvent Extraction of Petroleum Cresylic Acids

Feed Composition (160-240°C)

	Wt.%
Tar Acids	82.2
Mercaptans) Thiocresols Disulfides)	16.3
Neutral Oils	1.5

Extraction Conditions

	Vol. Ratio
Tar Acid Oil	1.0
60% Methanol	2.0
Hexane	4.5

Purity of Tar Acids

	Wt.%
Neutral Oils	0.05
Tar Bases (Pyridine)	0.05
Mercaptans) (Thiocresols) Disulfides)	0.012

Table 4

Removal of Dihydric Phenols From High Boiling Tar Acids
230-350°C

Extraction Conditions

Exp. No.	1	2	3
	Feed Rates (ml/min.)		
Tar Acids	4.5	4.5	4.5
Aqueous Methanol	12.0 (30%)	12.0 (35%)	18.0 (40%)
Hexane	10.5	10.5	10.5
Yields (Wt.% Tar Acid Feed)			
Methanol Extract	11	12	21
Hexane Raffinate	89	88	79

Table 5

Separation of 2,6-Xylenol From Mixed Cresols

Extraction Conditions

	Vol. Ratio	
Tar Acids	1	1
Aqueous Methanol	5 (45%)	10 (35%)
Hexane	10	5
Feed Composition		
o-Cresol	43.0	42.2
m-Cresol) p-Cresol)	40.0	42.5
2,6-Xylenol	17.0	15.3
Naphtha Raffinate Yield, (Wt.% Feed)	16.1	9.1
Composition, Wt.%*		
2,6-Xylenol	67.3	91.2
o-Cresol	19.1	8.8
m,p-Cresol	13.6	-

*Based on IR analysis.

FIGURE 1

FRACTIONAL SOLVENT EXTRACTION APPARATUS

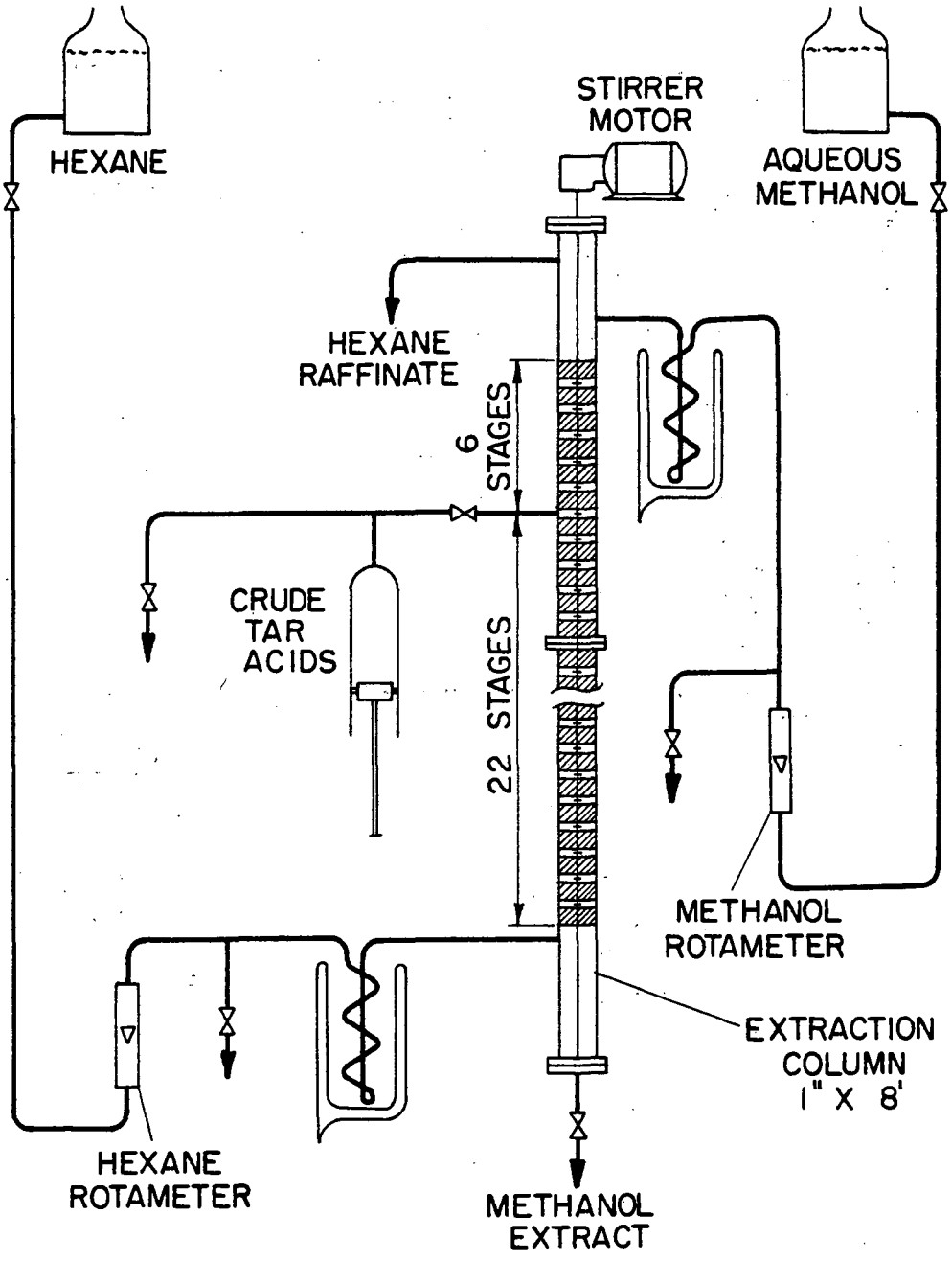
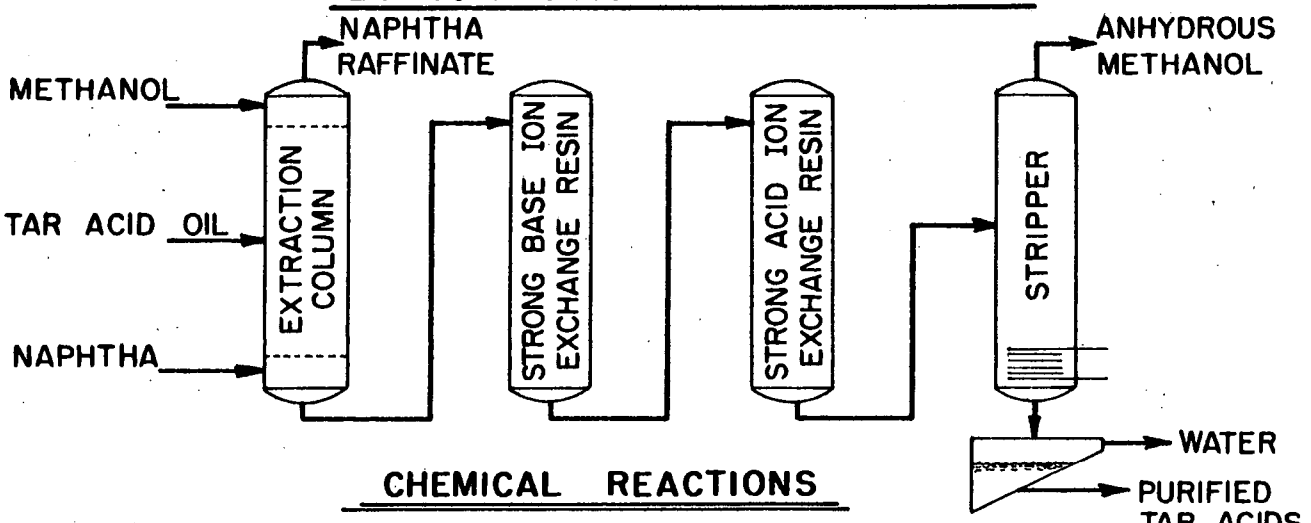


FIGURE 2

REMOVAL OF TAR BASES & ALIPHATIC ACIDS BY ION EXCHANGE REFINING



CHEMICAL REACTIONS

$$R_4N^+ OH^- + \emptyset OH \longrightarrow R_4NO\emptyset + H_2O$$

$$R_4N^+ OH^- + RCOOH \longrightarrow R_4NOOCR + H_2O$$

$$RSO_3H + \text{(pyridine)} \longrightarrow RSO_3^- \text{(pyridinium)} + H^+$$

PURITY OF TAR ACIDS (Wt. %)

NEUTRAL OILS	0.08
TAR BASES (PYRIDINE)	0.05
ALIPHATIC ACIDS	Nil